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Thermo-Analytical and Structural Characteristics of PDLCs Doped with Metal-Oxide Nanoparticles

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Abstract - Polymer Dispersed Liquid crystals (PDLCs) are materials with combined properties of polymers and liquid crystals (LCs). Phase diagrams of PDLC-nanoparticle composite systems using Differential scanning calorimetry (DSC) are investigated. Structural properties are studied by means of infrared spectroscopy. To utilize the size and shape dependent properties of nanoparticles (NPs) for LC applications, we doped (PDLCs) with metal-oxide nanoparticles [ZnO & γ-Fe_2O_3]. PDLCs are formed by dispersing micron-sized droplets of cholesteric liquid crystal in a matrix of poly (methyl methacrylate) (PMMA). FT-IR results shows increase in % transmission with increase in dopant concentration of ZnO nanoparticles, but variation in % transmission is minimal in case of γ-Fe_2O_3 nanoparticles doped samples. DSC results shows that lowest CPT is obtained for 0.5 % ZnO nanoparticles doped sample and 0.7 % γ-Fe_2O_3 nanoparticles doped sample.

Index Terms - *PDLCs, metal oxide nanoparticles, ZnO nanoparticles, γ-Fe_2O_3 nanoparticles, Thermo-analytical, Structural.*

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I. Introduction

Liquid crystals are materials having molecular orientation between solid crystals and isotropic liquid. It means they are the intermediate state between that of solid crystalline phase and isotropic liquid phase. Thermo-analytical behaviour of Thermotropic Liquid crystals molecules (also known as mesogens) shows various mesophases with change in temperature. The very important property of liquid crystals is their anisotropy which manifests in many different optical, electro-optical, dielectric, elastic properties. But no single substance will be able to give all the appropriate properties for a particular application. The unique properties of nanoparticles can be utilized to enhance these features. For a better understanding of the effects of nanoparticles from thermal and structural point view, we doped PDLCs with metal-oxide nanoparticles and investigated their phase diagrams with DSC and their structural properties were studied with the help of their infrared absorption spectra.

A. Iron Oxide Nanoparticles (γ-Fe2O3)/maghemite:

These are magnetic metal oxide nanoparticles. Magnetic nanoparticles are of great interest due to their applications in various disciplines like information/data storage, bio-sensing, biomedical, magnetic resonance imaging, drug delivery. Iron oxide nanoparticles are with diameters between about 1 to 100 nanometres. There are two main forms one is magnetite (Fe_3O_4) and its oxidized form maghemite (γ-Fe_2O_3). They have attracted extensive interest [9-10,16] due to their superparamagnetic properties and their potential applications in many fields (although Co and Ni are also highly magnetic materials, they are toxic and easily oxidized).

B. Zinc Oxide Nanoparticles (ZnO):

Zinc oxide is a unique material that exhibits semiconducting and piezoelectric dual properties. Nanostructured ZnO materials have key technological performance in electronics, optics and photonics. The biggest advantage of ZnO is that it is a versatile functional material that has a diverse group of growth morphologies, such as nanocombs, nanorings, nanohelixes/nanosprings, nanobelts, nanowires and nanocages. ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength opto-electronic applications. ZnO is transparent to visible light.

C. Materials Used.

We prepared PDLCs using Solvent-Induced phase separation (SIPS) method. LC- Cholesteryl propionate and Polymer-Poly (methyl methacrylate) is used to form polymer matrix. We doped thus prepared PDLCs by γ-Fe_2O_3 (20 nm - 50 nm) nanoparticles and Zinc Oxide (ZnO) (20 nm) nanoparticles in 4 different concentrations. Concentration of γ-Fe_2O_3 used for doping PDLCs in this present work are 0.01 %, 0.03%, 0.05 %, 0.07 %. Concentration of ZnO used for doping PDLCs in this present work are 0.2 %, 0.5%, 0.8 %, 1 %.

II. Experimental Details

A. Differential Scanning Calorimetry (DSC)

DSC measures the heats of transitions of the sample subjected to linear temperature ramp. This thermo-analytical technique gives the quantitative and qualitative information about the physical and chemical changes that involve exothermic (heat flows out of the sample) and endothermic (heat flows into the sample) processes. We investigated the

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pure PDLCs sample and metal-oxide nanoparticles doped PDLCs samples to study the phase transition temperatures using DSC. Phase transition temperatures (PTTs) and clearing point temperatures (CPT) are studied with the help of DSC. Clearing Point Temperatures (CPT) is a temperature at which anisotropic liquid crystal sample goes into isotropic state.

B. Fourier Transform Infrared Spectroscopy (FT- IR)

The goal of any absorption spectroscopy is to measure how well a sample absorbs light at each wavelength. FT-IR gives the absorption spectra over a wide range of wavelength. FT-IR is a preferred method for infrared spectroscopy. IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. We have employed this technique to observe any structural changes in the host PDLCs due to the doping of metal-oxide nanoparticles. Samples are investigated with wave number range from 400cm^{-1} to 4000cm^{-1}.

III. Results & Discussions

A. Results obtained from DSC Thermographs

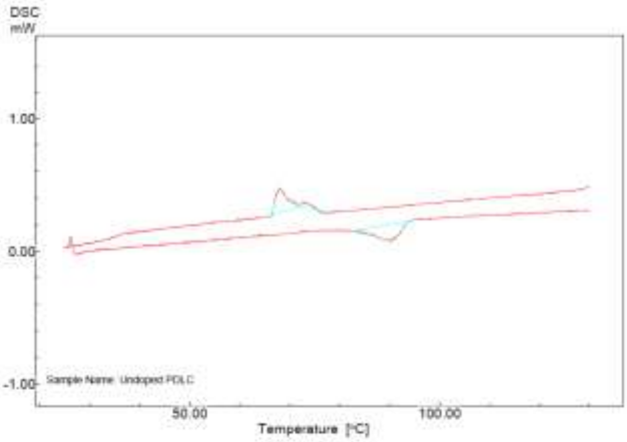

Fig. 1. Thermograph for Undoped PDLC

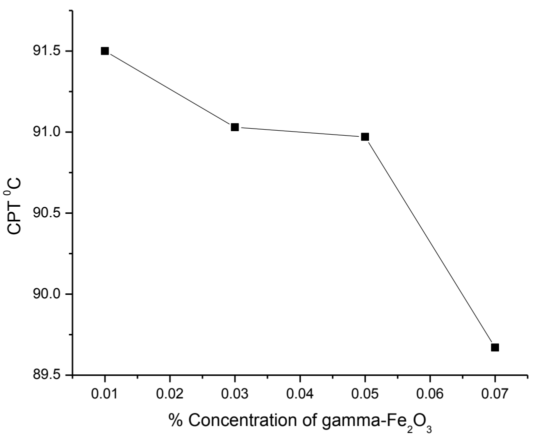

Fig. 2. Variation of CPT with % concentration of γ-Fe_2O_3 NPs

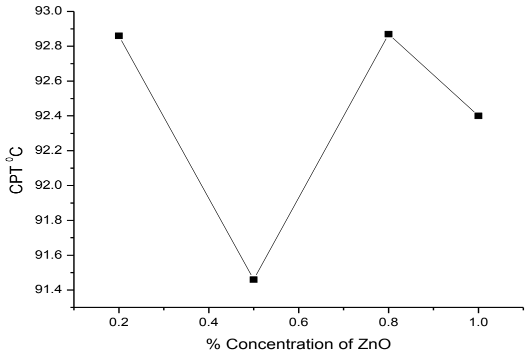

Fig. 12. Variation of CPT with % concentration of ZnO NPs

B. Discussions for the results obtained from DSC Thermographs

1) Thermograph for Undoped PDLC shows the phase transition temperature is obtained at 90.290C while heating and at 72.780C and 67.960C while cooling.
2) Clearing Point Temperatures (CPT) obtained from DSC for ZnO doped PDLC samples and for γ- Fe2O3 doped PDLC samples (except dopant concentration of 0.07% γ-Fe2O3) are higher than Undoped PDLC. This shows that the doped samples are more ordered than the undoped PDLC.
3) The CPT fluctuates with increase in dopant concentration of ZnO but lowest CPT is obtained for 0.5 % ZnO.
4) The CPT vs Concentration of γ- Fe2O3 nanoparticles graph shows that CPT decreases with increase in concentration of γ- Fe2O3. This helps us to conclude that LC phase stability of the sample doped with larger % of γ- Fe2O3 decreases with increase in the γ- Fe2O3 concentration. Lowest CPT is obtained for 0.07 % γ-Fe2O3 doped sample.
5) The CPT vs Concentration of ZnO graph shows that,PDLC+ZnO composite is more stable at 0.2% and 0.8% of ZnO than the other concentrations as they have higher CPT. This leads us to conclude that the composite is more ordered with these (0.2% and 0.8%) concentrations.

C. Transmission Spectra obtained from FT-IR Spectroscopy

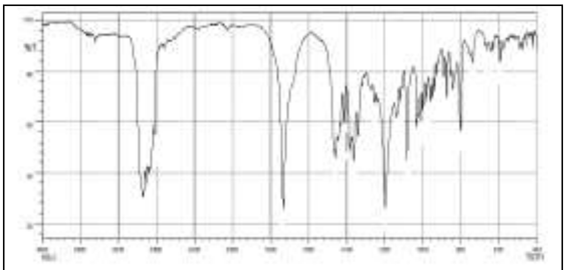

Fig. 3. Transmission Spectra for Undoped PDLC

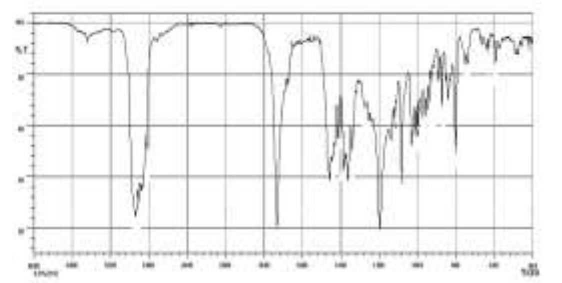

Fig.4. Transmission Spectra for 0.2 % ZnO doped PDLC

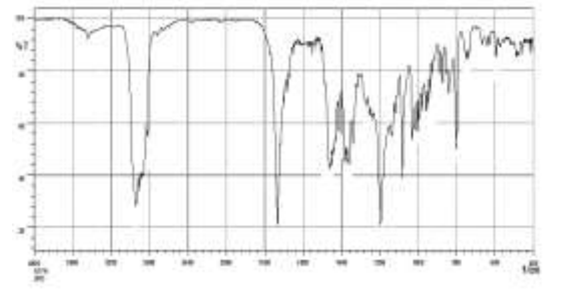

Fig.5. Transmission Spectra for 0.5 % ZnO doped PDLC

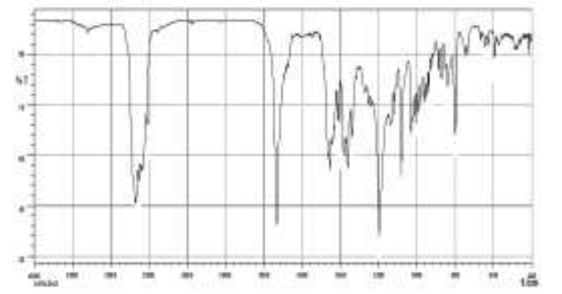

Fig.6. Transmission Spectra for 0.8 % ZnO doped PDLC

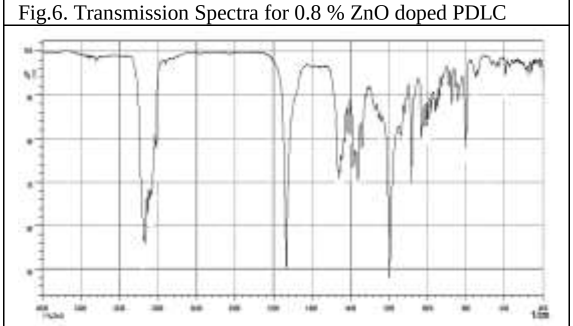

Fig.7. Transmission Spectra for 1 % ZnO doped PDLC

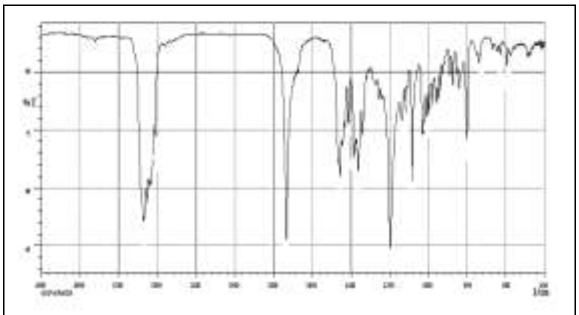

Fig.8. Transmission Spectra for 0.01 % γ-Fe_2O_3 doped PDLC

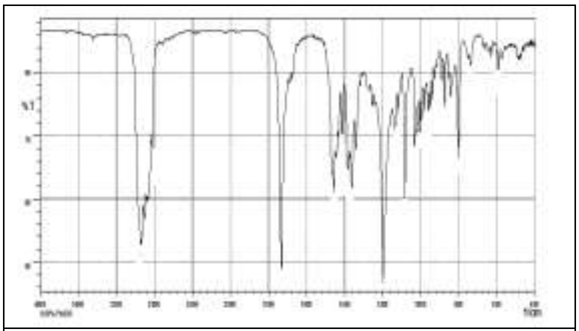

Fig.9. Transmission Spectra for 0.03 % γ-Fe_2O_3 doped PDLC

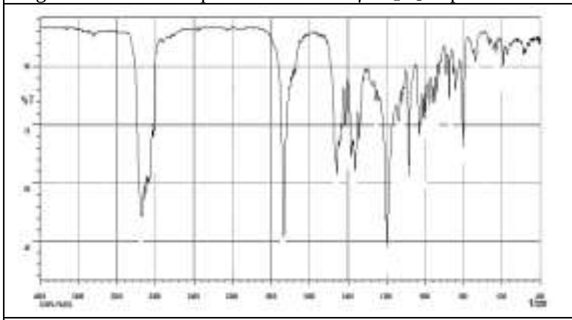

Fig.10. Transmission Spectra for 0.05 % γ-Fe_2O_3 doped PDLC

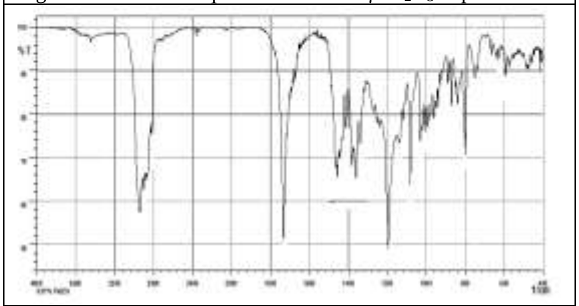

Fig.11. Transmission Spectra for 0.07 % γ-Fe_2O_3 doped PDLC

Table 1. Transmission peaks obtained from FT-IR spectra for undoped & doped samples

Sr.No.	**Frequency band (1/cm)**	**Bond details**	**Functional group**
1	690-515	C-Br Strech	Alkyl halides
2	1000-650	=C-H bend	Alkenes
3	1320-1000	C-O Strech	alcohols, esters, carboxylic acid,Ethers
4	1360-1290	N-O symmetric stretch	nitro compounds
5	1370-1350	C-H rock	Alkanes
6	1370-1390	Ch3 C-H bend	Alkanes and alkyls
7	1500-1400	C-C stretch (in ring)	Aromatics
8	1740-1720	C=O stretch	Aldehyde, saturated aliphatic
9	2830-2695	H-C=O:C-H strech	aldehydes
10	3000-2850	C-H stretch	alkanes

D. Discussions for the results obtained from FT-IR Spectroscopy

1) In case of γ-Fe_2O_3 doped samples it's observed that the variation in the peak intensity is very less with increase in the doping concentration.
2) Except for C = O bond functional groups, the peak intensity is decreasing. This shows that these functional groups are not suppressed due to the doping of γ-Fe_2O_3.
3) For ZnO doped samples there is an increase in the % transmission with the increase in doping concentration. This indicates that ZnO helps in molecular alignment of the LC molecules with respect to polymer.
4) The increase in % transmission thus leads us to conclude that the doping has further increased the homogeneity of the sample. It is observed that LCs has maintained their properties in spite of doping.

IV. Conclusion

Polymer dispersed liquid crystals are very novel materials pertaining to their applications in various fields. Also, Metal oxide nanoparticles represent a field of materials chemistry which attracts considerable interest due to the potential technological applications of these compounds. Due to the doping of nanoparticles, it is observed that clearing point temperatures vary with ZnO nanoparticles and decreases with γ-Fe_2O_3. Thus, we get different temperature ranges to use material in respective required temperature range applications. So, it is observed that nanoparticles doping enhances the properties of PDLCs. The spectra obtained from FT-IR reveals that LCs have maintained their properties in spite of doping. But do not show the structural changes.

References

[1] Gupta Sureshchandra, J., et al. (2000). ‘‘Phase Transition Temperatures of LCs using Fabry-Perot Etalon’’ Molecular Crystals; Liquid Crystals, Procs of ILCC 2000, Japan, Vol. 364–368.

[2] Gupta Sureshchandra, J., (2000). Liquid Crystals: Chemistry, Physics and Applications, (Proceedings of SPIE, Poland), 4147 23.

[3] Gupta Sureshchandra J, “Indian J of Pure Appl Phys”,37 620 (1999)

[4] Gupta Sureshchandra J, “J of Optics”,29 pp 53-62(2000)

[5] Gupta S J, Gharde R A and Tripathi A R,”Molecular Crystals & Liquid Crystals”, (Procs. Of ILCC2000, Japan) 364 461 (2000).

[6] J.L west and R Ondris-Crawford, “Characterization of polymer dispersed liquid-crystal shutters by ultraviolet/visible and infrared absorption spectroscopy”,J.Appl.Phys, 70(7),pp 3785-3790

[7] Oleg V. yaroshchuk,et. al, “Electroptics and Structural Peculiarities of Liquid crystal nanoparticle-polymer composites” Physical Review E 72, 051715(2005).

[8] TOPICAL REVIEW: Zinc oxide nanostructures: growth, properties and applications, Zhong Lin Wang, J. Phys.: Condens. Matter 16 (2004) R829–R858

[9] Review: Tuning the Magnetic Properties of Nanoparticles, *Int. J. Mol. Sci.* **2013**, *14*(8), 15977-16009;

[10] Superparamagnetic iron oxide nanoparticles (SPIONs): Development, surface modification and applications in chemotherapy, Elsevier: Advanced Drug delivery reviews, 2011, Pages 24–46

[11] John Coates, Interpretation of Infrared Spectra, A practical approach, Encyclopedia of Analytical Chemistry,pp 10815-10837,John Wiley & Sons,2000.

[12] Liquid Crystals- I.C.Khoo, John Wiley & Sons, (2007).

[13] Liquid Crystals -Natures Delicate Phase- Peter J. Collings

[14] www.corrosionlab.com/facilities/ftir-interpretation.htm

[15] http://www.sigmaaldrich.com/technical-documents/articles/technology-spotlights/iron-oxide-nanoparticles-characteristics-and-applications.html